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A Robust Process for Biodiesel Production Using Supercritical Methanol

An Undergraduate Honors College Thesis

in the

Ralph E. Martin Department of Chemical Engineering
College of Engineering
University of Arkansas
Fayetteville, AR

by

Meagan Magie

April 2009

Meagan Magie

Honors Thesis

The project I worked on to fulfill my honors thesis requirements was “A Robust Process for Biodiesel Production Using Supercritical Methanol.” Nine of my classmates and I participated in the Environmental Protection Agency’s P3: People, Prosperity, and the Planet Sustainability competition, where we presented our work at the National Design Expo in Washington D.C.

I was the team leader of our ten member team. As the team leader, I was responsible for running the meetings, assigning specific jobs for all team members, overall organization of our project, and keeping everyone on task with their assignments.

I was involved in all areas of our project, which included research and literature review, design and construction of our supercritical methanol reactor, algae oil extraction, experimental and laboratory testing, and writing a paper summarizing our project. However, I spent the majority of my time writing the summary of our phase I project and a proposal for continued research during phase II. I also worked to create partnerships that were vital to the success of our project.

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I. Executive Summary

Date of Project Report: 23 March 2009

EPA Agreement Number: SU833926

Project Title: A Robust Process for Biodiesel Production Using Supercritical Methanol

Faculty Advisors, Departments, and Institutions:

Robert Babcock, Chemical Engineering, University of Arkansas at Fayetteville
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William Roy Penney, Chemical Engineering, University of Arkansas at Fayetteville
Greg Thoma, Chemical Engineering, University of Arkansas at Fayetteville

Student Team Members, Departments, and Institutions:

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Travis Roberts, Chemical Engineering, University of Arkansas at Fayetteville
Josh Robinson, Chemistry, University of Arkansas at Fayetteville
Andrew Wolfe, Chemical Engineering, University of Arkansas at Fayetteville

Project Period: August 2008 – April 2009

Description and Objective of Research:

The overarching purpose of Phase I was to test, at the bench scale, a continuous supercritical methanol reactor, and to determine the feasibility of implementing the technology at full scale. Specific objectives in reaching this purpose included:

Objective 1: *Choose a viable feedstock*

Objective 2: *Perform experiments for oil extraction*

Objective 3: *Design, build and operate a continuous supercritical methanol reactor*

Objective 4: *Design and simulate full scale biodiesel facility*

Objective 4a: *Perform life-cycle and economic analysis on full scale design*

Objective 5: *Prepare a Phase II P₃ project to demonstrate the entire biodiesel process*

Project Scope: *The students performed extensive review of the literature regarding both feedstock selection and alternate conversion technologies. After the system was designed and constructed, the students performed all experiments in the laboratory.*

Summary of Findings (Outputs/Outcomes):

A literature review was conducted in order to insure the feedstock choice had the potential to bring about positive impacts in making progress toward sustainability. The use of

algae for a biodiesel feedstock was chosen for the many benefits it provides. Algae produced via the ATS system removes carbon dioxide from the atmosphere, removes nutrients from polluted water, provides opportunity for production of other bio-fuels (e.g., butanol or ethanol from the cellulosic component of the algae) and environmentally friendly fertilizers, and decreases the consumption of fossil fuel.

Experiments were performed to determine the most effective method for extracting algae oil through their virtually indestructible cell walls. The following methods were tested: mortar and pestle, Waring blender, hexane extraction alone, salt-water solution, glycerol solution, and urea solution. It was ultimately concluded that lysing the cells with an osmotic shock using glycerin would be the most effective method to release the oil for extraction with hexane. The fraction of oil extracted, on a dry solids basis ranged from 0.37% to 2.67%. The mortar and pestle method gave the highest yield of 2.67%. Unfortunately, the mortar and pestle method requires dried algae and grinding of dry algae; thus, costs on are prohibitive for a full scale plant. The least effective method, surprisingly, was using an 8 M urea solution to weaken the cell wall hydrogen bonds; we believe this is because there is a relatively low quantity of cellulose in the algae cell wall. Salt and glycerol solutions utilize osmotic shock as the cell disruption mechanism. The salt solution was actually more effective than the glycerol, yielding 2.53% vs. 2.2%. However, salt solution lysing is not practical for a full scale plant design because the salt must be recycled and the cost of removing water required for salt recycle is prohibitive.

Constructing a reactor that can run continuously is only a small part required to prove the viability for producing biodiesel at a larger level; however, the ability to create such a reactor provides evidence that the chosen technology has potential for being implemented on a full scale. Students at the University of Arkansas designed and built a continuous supercritical methanol reactor for the production of biodiesel from commercially available materials. The continuous supercritical methanol reactor is one of the first of its kind. The reactor was tested with a variety of triglyceride (TGly) and free fatty acid (FFA) feedstocks to demonstrate its robustness. The experimental runs proved that high conversion, ranging from 60% to 85%, could be obtained with feeds ranging from 100% FFA to 100% triglycerides.

A full scale simulation was designed using Pro II process simulation package. The material and energy balance information provided by the simulation allowed students to perform a streamlined life cycle analysis. Because glycerin is used to lyse the algae cell, and it is not economical to recover and recycle the glycerin, it is sent with the algae biomass to an anaerobic digester where methane is produced and used on site for heating needs; the excess is sold off site, and an avoided product credit is claimed for this natural gas. Due to the very heavy use of glycerin, this process does not yet make positive environmental impacts compared to alternative biodiesel production methods. If a source of waste glycerin can be found, it would not carry an environmental burden into this process, and the algae biodiesel becomes very favorable. This highlights the reason that algae have not yet become a viable alternative feedstock: it is extremely difficult to extract the oil. This also points clearly to the need for additional research in this area.

Although it is well known that a full scale process to produce biodiesel from algae is not economical as an industrial commercial venture with the current technology, the team evaluated the venture as a government funded project and determined that the project is revenue neutral; i.e., the venture does not cost the taxpayers. The proposed demonstration plant provides 71 permanent, high paying jobs in addition to removing fossil fuel from our fuel mix, which reduces CO₂ emissions. The proposed capital estimate of the commercial scale plant is

summarized below. The algal growing ponds cost \$25,000,000 and the total installed cost of other equipment is \$15,000,000, giving a total capital cost of \$40,000,000. The project is essential to our economic and national security; thus, it should be financed with the sale of US Treasury Bonds bearing an interest rate of 4.00% p.a. for 30 years. After the bonds mature in 30 years, additional bonds will be sold to repay the original bondholders. The yearly interest on the bonds is \$1,620,000 will be paid by the venture, resulting in no net cost to the US taxpayers.

Conclusions:

This P₃ Phase I project defines a scenario for producing fuels (biodiesel) from a renewable resource (algae) which will, with further research to improve extraction of oil from the algae, benefit people, improve economic prosperity, and eventually reduce the impact of economic activity on global warming by reducing the emissions of CO₂ from use of fossil fuel diesel.

The original objective of the P₃ project was to investigate the technical and economic feasibility of utilizing a high pressure, high temperature supercritical methanol reactor to esterify, hydrolyze and transesterify fatty acids and triglycerides (the components of algae oil). This objective was achieved and, additionally, a pilot plant unit was designed for Phase II, a preliminary design was completed for a full scale demonstration plant and a life cycle and economic analysis were accomplished.

Integration of P₃ Concepts as an Educational Tool

Nine Chemical Engineering Seniors and 1 Chemistry Senior, the GREENIES (Generating Renewable Energy for Economic Nourishment and Improvement of Environmental Sustainability) team, have participated in this Phase I P³ sustainability competition. The chemical engineering students are participating to fulfill their course requirements for the chemical engineering capstone senior design course and the chemistry major is receiving course credit for a technical elective. This P³ project satisfied more than the requirements of the capstone design course, which includes performing heat and mass balances; preparing process flow diagrams; designing, scaling-up and costing process equipment; performing economic analysis and using the latest and best process simulators. This competition allowed the students to obtain extremely valuable experience with laboratory experimentation, which is not a normal part of the capstone design. Additionally, the organic chemistry component of the P³ was excellent. The hands on experience of designing and building experimental equipment apparatuses from scratch, conducting experiments, analyzing samples and presenting results are part of the invaluable experience which this P³ project offered.

The GREENIES designed a full-scale demonstration plant to produce biodiesel. The economics of this plant were determined. Using the demonstration plant economics as a basis, a life-cycle analysis was performed. This project linked knowledge from all undergraduate courses into the design of a demonstration plant which could have far reaching outcome to provide people renewable energy, while prospering and helping save the planet from global warming.

Proposed Phase II Objectives and Strategies:

As part of the work completed in Phase I, a bench scale continuous supercritical methanol (SCM) reactor was built from commercially available components. The reactor produced biodiesel at 16mL/minute. The utilization of this robust process offers developed and developing nations the capability of producing a renewable, non-petroleum based diesel fuel.

The ability of the supercritical methanol process to handle feedstocks with diverse compositions, without the use of a catalyst sets this technology apart from other biodiesel production methods.

Phase I also included detailed research of feedstock options. It was desired to choose a feedstock that could offer a sustainable alternative to the use of fossil fuels and demonstrate the diversity of the supercritical methanol process. After a thorough investigation, algae oil was chosen as a feedstock because of its ability to satisfy these desires. As discovered during Phase I, algae can be used successfully to remove nutrients from polluted water streams while absorbing carbon dioxide from the atmosphere providing significant environmental benefits. The use of algae can also illustrate the importance of the supercritical methanol process because of the differing oil composition contained in the multiple different species of algae that exist. For Phase II, the technical challenges include (1) improving the efficiency of algae oil extraction yield; (2) optimizing the reactor operation with multiple runs; and (3) finalizing a design to produce biodiesel from algae. To address sustainability implementation, students will (1) develop a economic analysis for implementation of a full scale facility (1MM gallons per year) on the Mississippi River; and (2) perform a life-cycle analysis for this facility.

Partnerships have already been developed with corporations utilizing Algal Turf Scrubbing (ATS) in Maryland and Florida. Building on those relationships, students working on Phase II will work alongside Biological Engineers at the University of Arkansas to help harvest algae from a recently built ATS system in Springdale, Arkansas. These students will travel to the Springdale facility, 15 miles away from the University of Arkansas campus, on a weekly basis to harvest the algae biomass. Because the quantity of biomass produced by the ATS system in Springdale is limited, algae will also continue to be collected from partners in Florida and Maryland. Mark Zivojnovich, vice president of project development at HydroMentia Inc., has agreed to supply Phase II with enough algae necessary to test and run the extraction unit that is proposed.

Publications/Presentations: none

Supplemental Keywords: biodiesel, supercritical methanol, algae, renewable, sustainable, energy, environment, alternative fuel

Relevant Web Sites: <http://www.hydromentia.com/>

II. BODY OF REPORT

A. Summary of Phase I Results

Background and Problem Definition

As natural resources are being overly consumed by the growing population, a renewable fuel source is needed for a more sustainable energy infrastructure. Biodiesel is a non-petroleum based fuel composed of alkyl esters from renewable feedstocks. Our planet will only prosper long term if efficient means are developed to convert sunlight, atmospheric CO₂ and limited supplemental nutrients to fuels. The widespread success of biodiesel as an alternative, renewable liquid fuel has been hampered by several factors. These include the requirement for a locally available feedstock, feedstock quality and consistency from day to day, and lack of sufficient infrastructure for the delivery of the product to a wide market. With these technical and engineering challenges at hand, a robust process is needed to handle the variety of oily feedstock that may be available in any given locality. Developing technologies like this will foster economic prosperity through creation of high quality technical jobs.

Choice of an appropriate chemistry for conversion of oils to biodiesel is a critical decision in all biodiesel projects. After a thorough review, supercritical methanol (SCM) conversion technology was found to be the most robust approach for producing biodiesel because of its ability to convert both free fatty acids (FFA) and triglycerides (TGly), without the use of a catalyst. The challenge of Phase I was to construct a bench scale and design full scale implementation of the supercritical methanol technology.

Another important component was choosing a suitable feedstock. Algae is the feedstock which meets most ideal requirements: it is the most efficient mechanism on earth to convert sunlight, atmospheric CO₂ and limited supplemental nutrients to fuel feedstock; it grows fast and steadily, must be harvested often and grows even on non-arable lands, thus avoiding the fuel vs. food issue.

The primary technical problem of algae to biodiesel is to put into place the myriad components required to grow algae, harvest it, extract the oil and efficiently convert the oil to biodiesel. The current Phase I P³ project followed by the proposed Phase II will put all the pieces of the puzzle together and define a commercial algae oil to biodiesel project which will provide permanent jobs and an ongoing demonstration project which will further allow continued improvement of the technology with the ultimate goal of private enterprise implementation.

Relationship to People, Prosperity, and the Planet

The primary aim of the work for Phase I was to design a process that would integrate and sustain environmental protection, economic prosperity, and social benefit. With these tasks in mind, students designed a process to produce biodiesel using algae oil. This process provides a renewable, biodegradable fuel source that decreases sulfur and particulate-matter emissions and reduces the United State's dependence on foreign oil¹⁷. Biodiesel also provides lubrication for better-functioning mechanical parts and has excellent detergent properties¹⁷. The use of algae oil for the production of biodiesel not only has the ability to lessen carbon emissions, but this process also completes the carbon cycle as the limiting amount of carbon emitted into the atmosphere by diesel engines is recaptured by the algae.

Relevance and Significance to developing or developed world

Changing the energy infrastructure from fossil fuels to bio-fuels provides significant benefits for developed countries, such as the United States. With the implementation of biodiesel production, the U.S. will reduce its dependency on unreliable, expensive foreign fuel sources while creating domestic labor and market opportunities. A transition into bio-fuels also creates a renewable fuel source. This full scale biodiesel production system is also capable of being utilized in underdeveloped areas. If employed in developing countries, the ATS system has the ability to clean polluted streams, as well as provide jobs and fuel source where there are no funds to purchase foreign petroleum.

Integration of P3 Concepts as an Educational Tool

Nine Chemical Engineering Seniors and 1 Chemistry Senior, the GREENIES (Generating Renewable Energy for Economic Nourishment and Improvement of Environmental Sustainability) team, have participated in this Phase I P3 sustainability competition. The chemical engineering students are participating to fulfill their course requirements for the chemical engineering capstone senior design course and the chemistry major is receiving course credit for a technical elective. This P3 project satisfied more than the requirements of the capstone design course, which includes performing heat and mass balances; preparing process flow diagrams; designing, scaling-up and costing process equipment; performing economic analysis and using the latest and best process simulators. This competition allowed the students to obtain extremely valuable experience with laboratory experimentation, which is not a normal part of the capstone design. Additionally, the organic chemistry component of the P3 was excellent. The hands on experience of designing and building experimental equipment apparatuses from scratch, conducting experiments, analyzing samples and presenting results are part of the invaluable experience which this P3 project offered.

The GREENIES designed a full-scale demonstration plant to produce biodiesel. The economics of this plant were determined. Using the demonstration plant economics as a basis, a life-cycle analysis was performed. This project linked knowledge from all undergraduate courses into the design of a demonstration plant which could have far reaching outcome to provide people renewable energy, while prospering and helping save the planet from global warming.

Purpose, Objectives, Scope

The overarching purpose of Phase I was to test, at the bench scale, a continuous SCM reactor, and to determine the feasibility of implementing the technology at full scale. Specific objectives in reaching this purpose included:

Objective 1: *Choose a viable feedstock*

Objective 2: *Perform experiments for oil extraction*

Objective 3: *Design, build and operate a continuous supercritical methanol reactor*

Objective 4: *Design and simulate full scale biodiesel facility*

Objective 4a: *Perform life-cycle and economic analysis on full scale design*

Objective 5: *Prepare a Phase II P3 project to demonstrate the entire biodiesel process*

Project Scope: *The students performed extensive review of the literature regarding both feedstock selection and alternate conversion technologies. After the system was designed and constructed, the students performed all experiments in the laboratory.*

Data, Findings, Outputs/Outcomes

Table 1 provides a compilation of data including the advantages and disadvantages of biodiesel production methods. The team decided that SCM held the most potential as a robust technology because it can equally well handle both free fatty acids and triglycerides.

Table 1. Advantages and Disadvantages of Biodiesel Production Methods¹⁷

Biodiesel Production Method	Advantages	Disadvantages
Base-Catalyzed Transesterification	<ul style="list-style-type: none"> • Proven • Low temperature, ambient pressure • Short reaction times with triglycerides • Low methanol: oil ratio (~6) 	<ul style="list-style-type: none"> • Inhibited by FFA contents >.5% • Requires refined feedstocks • Product separation difficulties • Catalyst neutralization/recovery
Acid-Catalyzed Esterification	<ul style="list-style-type: none"> • Proven • Low temperature, ambient pressure • Short reaction times with FFA • Effective pretreatment for high FFA feedstocks 	<ul style="list-style-type: none"> • Inhibited by water • High methanol:oil ration (~40) • Slow reaction with triglycerides • Catalyst neutralization/recovery • Corrosion-resistant materials required
Enzyme Catalysis	<ul style="list-style-type: none"> • Low temperature, low pressure • Treats FFA and triglycerides • Essentially pure product, no by-products • Simple product recovery • Low methanol: oil ratio (~4) 	<ul style="list-style-type: none"> • Long reaction time • Expensive enzymes • Enzyme inactivation (water)
Hydroprocessing	<ul style="list-style-type: none"> • Proven • Treats FFA and triglycerides 	<ul style="list-style-type: none"> • High temperature, moderate to high pressure • Pretreatment/Post-treatment (isomerization) • Eliminates beneficial properties • Catalyst coking, poisoning, regeneration • By-products
Supercritical Methanol Treatment	<ul style="list-style-type: none"> • Treats FFA and triglycerides • No catalyst required • Not inhibited by water • Simple product separation • Short reaction times 	<ul style="list-style-type: none"> • High temperature, high pressure without cosolvent • Moderate to high methanol:oil ratio (~15)

Choose viable feedstock

A literature review was conducted in order to insure the feedstock choice had the potential to bring about positive impacts in making progress toward sustainability. The use of algae for a biodiesel feedstock was chosen for the many benefits it provides. Algae produced via the ATS system removes carbon dioxide from the atmosphere, removes nutrients from polluted water, provides opportunity for production of other bio-fuels (e.g., butanol or ethanol from the cellulosic component of the algae) and environmentally friendly fertilizers, and decreases the consumption of fossil fuel. As the demand for energy increases, the development of a renewable fuel sources is an important component of sustainable consumption through the reduction of our dependence on non renewable fossil fuels which will be beneficial to future generations. The use of algae as a feedstock also benefits society because it is not competing with food sources such as soybean and corn oil; in addition, algae can be cultivated on marginal land that would otherwise not be suitable for crop production. Furthermore, algae are more productive than terrestrial crops, with mean yearly rates in the central U.S. being 30-40g (dry)/m²/day. Traditional crop production in the U.S. is 2-4g (dry)/m²/day. At the same levels of light, algae can photosynthesize and produce new tissue at roughly 10 times that of typical crops¹.

Algae oil extraction

Students established a relationship with HydroMentia, which holds the industrial license for the Algal Turf Scrubber (ATS), who have provided samples of algae from one of their Florida facilities. Experiments were performed to determine the most effective method for extracting algae oil through their virtually indestructible cell walls. The following methods were tested: mortar and pestle, Waring blender, hexane extraction alone, salt-water solution, glycerol solution, and urea solution. The most cost effective for commercial application was glycerol solution lysing, which ruptures cell wall by osmotic pressure differences.

Table 2 presents results of all the extraction experiments. The fraction of oil extracted, on a dry solids basis ranged from 0.37% to 2.67%. The mortar and pestle method gave the highest yield of 2.67%. Unfortunately, the mortar and pestle method requires dried algae and grinding of dry algae; thus, costs on are prohibitive for a full scale plant. The least effective method, surprisingly, was using an 8 M urea solution to weaken the cell wall hydrogen bonds; we believe this is because there is a relatively low quantity of cellulose in the algae cell wall. Salt and glycerol solutions utilize osmotic shock as the cell disruption mechanism. The salt solution was actually more effective than the glycerol, yielding 2.53% vs. 2.2%. However, salt solution lysing is not practical for a full scale plant design because the salt must be recycled and the cost of removing water required for salt recycle is prohibitive. The laboratory procedure which could most effectively be implemented in the pilot plant is:

1. Blend 1 kg of wet algae in a Waring blender to break clumps.
2. Add 1kg of 20% glycerol solution and agitate for 10 minutes.
3. Add 500 mL of hexane and agitate for additional 5 to 10 minutes.
4. Centrifuge in 250 mL tubes at approximately 600g for 15 minutes.
5. Decant the top hexane phase using a pipette.
6. Evaporate the hexane in a double boiler apparatus and collect the product when complete.

Algae extraction literature³ indicates various algal strains contain 2% to 40% oil on a dry basis. Obviously the strains of algae from Florida contain less than normal oil because the mortar and pestle technique should give extraction efficiencies above 90%. The strains tested were likely grown under unstressed conditions which give the lowest oil yields. As an economic premise for plant scale economics it was assumed that 5% yield of oil could be achieved with moderate optimization.

Table 2. Extraction Experiment Results

Method of Preparation	Salt Water Concentration (m/m)	Glycerol/ Water (g)	Glycerol/Water Concentration (m/m)	Urea Solution (mL)	Urea (M)	Wet Algae (g)	Dry Algae (g)	Oil (g)	Oil (%/dry mass)
1. Hood dried 2. Added water and mixed in Blender	x	x	x	x	x	1171.88	187.5	0.7	0.37%
1. Hood dried 2. Mortar and pestle 3. Added Water and mixed in Blender 4. Sonicated for 1 hour	x	x	x	x	x	828.75	132.6	1.1	0.83%
1. Hood dried 2. Mortar and pestle 3. Added Water and mixed in Blender	x	x	x	x	x	626.25	100.2	0.9	0.90%

1. Hood dried 2. Mortar and pestle 3. Added water and mixed in blender 4. Added salt water to algae mixture	0.5	x	x	x	x	1578.75	252.6	2.5	0.99%
1. Mixed in blender 2. Added salt water to algae mixture	0.5	x	x	x	x	790.4	55.3	1.4	2.53%
1. Mixed in blender 2. Added glycerol to algae mixture	x	500	0.5	x	x	615.8	43.1	0.9	2.09%
1. Hood dried 2. Crushed in blender 3. Further crushing with mortar and pestle	x	x	x	x	x	824	82.4	2.2	2.67%
1. Mixed in blender 2. Added 20% glycerol solution to algae mixture	x	202.2	0.2	x	x	199.5	14	0.3	2.15%
1. Mixed in blender 2. Added urea to algae mixture	x	x	x	203.4	8	206.3	14.4	0.1	0.69%

Continuous supercritical methanol reactor

Constructing a reactor that can run continuously is only a small part required to prove the viability for producing biodiesel at a larger level; however, the ability to create such a reactor provides evidence that the chosen technology has potential for being implemented on a full scale. Biodiesel production via the supercritical methanol process has been performed in a batch reactor by a recent master's student at the University of Arkansas, but the process has not been widely researched or developed for a continuous reactor.

Students at the University of Arkansas designed and built a continuous supercritical methanol reactor for the production of biodiesel from commercially available materials. This continuous supercritical methanol reactor is one of the first of its kind. A photograph of the reactor is shown in Figure 1, and a process flow diagram of the experimental apparatus is included in Figure 2.

The experimental apparatus consists of three sections: the pre-treatment section, the reaction section, and the cooling section.

In the pre-treatment section of the process, two 100 mL feed vessels are used to hold the reactants. One vessel contains methanol at room temperature and the other contains oil heated and insulated with heat tape. Each fluid flows out of their respective containers through a fuel filter and into separate high pressure pumps. The pumps increase the pressure from atmospheric (14.7 psi) to 2000 psi. As the fluids exit their individual pumps, they flow through 1/8" diameter 316-stainless-steel tubing, where they meet and begin to mix at a tee. The mixed streams then enter the reaction section of the process.

In the reaction section, the pressurized mixture flows through the reactor which is made of 3/8" diameter static mixers. The static mixers are fitted with 90° angle compression fittings to form a rectangular coil. This reactor is housed in a 6 in. x 6 in. x 18 in. stainless-steel tank. The tank is filled with sand which acts as a heat transfer medium to homogenize the temperature of the reactor. Electrical strip heaters are attached to the outside wall of each side of the tank and

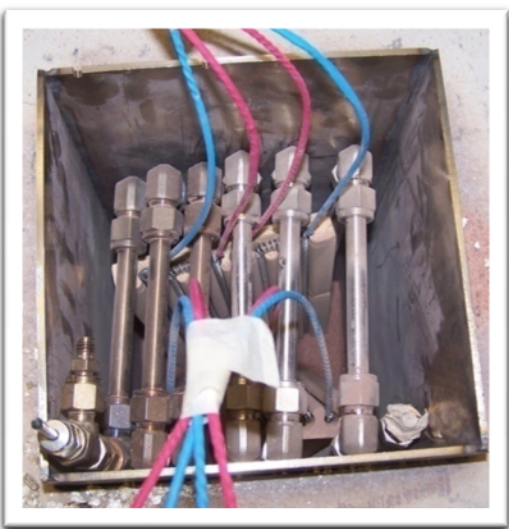


Figure 1. Supercritical Methanol Esterification/Transesterification Reactor

high pressure needle valve and into a regulator that reduces the pressure from 2000 psi to atmospheric pressure. Once the pressure has been blown down, the final product is collected in a beaker; it consists of two immiscible layers. The top layer is a methanol water mixture saturated with oil and the bottom layer is a biodiesel layer saturated with methanol. The bottom layer can be removed using a separatory funnel. This biodiesel layer is then heated to 70 °C to vaporize the methanol, leaving the biodiesel product.

The supercritical methanol reactor was tested with a variety of triglyceride and free fatty acid feedstocks to demonstrate its robustness. The experimental runs proved that high conversion could be obtained with feeds ranging from 100%

FFA to 100% triglycerides. In order to produce methyl-esters from triglycerides, water had to be added to the system to break the FFA from the glycerin backbone resulting in one glycerin molecule and three FFA molecules per triglyceride molecule. The three FFA molecules were then converted to methyl-esters by means of esterification. The product formed two distinctive layers, with one layer containing primarily biodiesel and unreacted oil and the other composed of water, glycerin, and excess methanol.

The biodiesel product was tested to confirm that it met ASTM fuel standards. The two layers were separated, via separatory funnel. The separated layers were analyzed to determine

the temperature is maintained at 350° C. The steel tank is housed in a ½" thick concrete box filled with vermiculite for insulation. The mixture leaves the reaction tank, flows past a thermocouple and then enters the cooling section of the process.

The cooling section of the process is where the product from the reaction section is cooled so it can be collected. As the fluid exits the reactor through the last static mixer, the flow continues into a 20" long section of 1/8" diameter 316-SS tubing. The stainless steel tubing passes through copper tubing. The double pipe heat exchanger cools the product stream. After the fluid has been cooled, the product can be collected. The pressure of the fluid is monitored with a pressure gauge as it flows through a

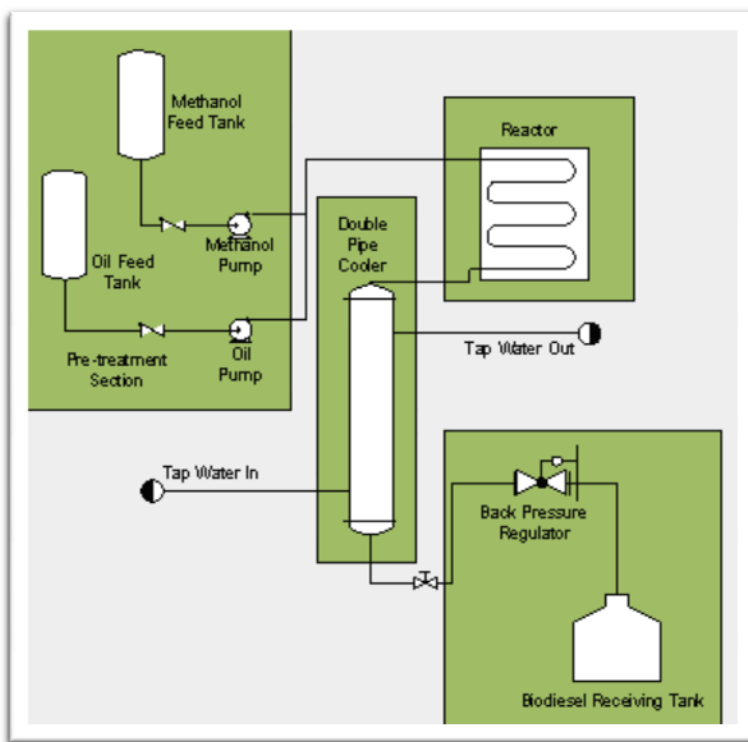


Figure 2. Experimental Apparatus for Continuous Biodiesel Production Using Supercritical Methanol

their compositions and chemical properties. The top phase was analyzed using a gas chromatograph equipped with a thermal conductivity detector to determine the amount of water and methanol present. The percent methanol in the top layer ranged between 70-90% depending on the feedstock. A boiling point distribution apparatus was used to distill the more volatile components from this layer, leaving behind any unreacted oil present in this phase. The bottom phase, which contained primarily biodiesel, was then distilled to remove any water or methanol. A gas chromatograph equipped with a flame ionization detector was used on the bottom phase to determine the percent of methyl esters present in this layer. In addition to the use of gas chromatography, a pynchnometer and Cannon-Fenske viscometer were used to determine the density and viscosity of the biodiesel. These values were then compared with ASTM standards to ensure they met the guidelines. The results of these tests are displayed in Table 3.

Table 3. Supercritical Methanol Reaction Experimental Results

Feed Composition		Biodiesel Viscosity (cSt)	Biodiesel Specific Gravity (g/ml)	Percent Conversion (mole basis)	Residence Time (min)	Water Added
Triglycerides (%)	Free Fatty Acids (%)					
0	100	3.48	0.854	78%	10	no
0	100	4.50	0.884	80%	10	no
0	100	3.20	0.885	75%	6	no
50	50	15.2*	0.902	60%	10	no
50	50	7.20	0.885	84%	10	yes
100	0	--	--	0%	10	no
100	0	--	0.920	68%	10	yes

*Sample was not visually homogeneous and was probably not pure biodiesel

These results demonstrate that the SCM method is robust with respect to feedstock; good yields were achieved over a range of feedstock compositions. This is important because algae feedstock will have variable composition of FFA and TGly as a function of the specific strains being grown, the season and the degree of nutrient stress. Analysis of algae samples contained from Florida, for instance, show 95% TGly. Further, it is important that most of the produced algae samples fell within the ASTM standard for biodiesel (viscosity between 1 to 6.3 cST) with very short residence times.

Designed and simulated full scale demonstration facility

A full scale simulation was designed using Pro II process simulation package. The material and energy balance information provided by the simulation allowed students to perform a streamlined life cycle analysis.

Performed life-cycle analysis on full scale design

An LCA was performed for the demonstration scale process using SimaPro® software with the EcoInvent inventory database, which relies heavily on data from EU processes. The infrastructure for the construction of the algae ponds was included in the LCA because of the large impact it will have on the overall energy picture. Credit was taken for the nitrogen and phosphorus removed from the river; these were simulated as negative pollutant emissions to water. ISO 14044 suggests that if allocation is necessary, that the use of avoided products is preferred over economic and mass allocation. We assumed that inorganic fertilizer is an avoided

product because the left over biomass from the process will have high N and P content, and can be used as a fertilizer. Because glycerin is used to lyse the algae cell, and it is not economical to recover and recycle the glycerin, it is sent with the algae biomass to an anaerobic digester where methane is produced and used on site for heating needs; the excess is sold off site, and an avoided product credit is claimed for this natural gas. The results of the SimaPro model for the system are presented in the figure below. Because of the very heavy use of glycerin, this process does not yet make positive environmental impacts compared to alternative biodiesel production methods. The assumed source for the glycerin in this process model is from a vegetable oil biodiesel plant; 10% of the production burden from that facility was assumed to be attributed to the glycerin. This is based on the observation that the glycerin co-product represents both approximately 10% of the mass of product and 10% of the value of products from a vegetable oil biodiesel facility. If a source of waste glycerin can be found or the extraction method improved, it would significantly reduce the environmental burden, and algae biodiesel becomes very favorable. This highlights the reason that algae are not yet a viable feedstock: it is extremely difficult to extract the oil. This also points clearly to the need for additional research in this area.

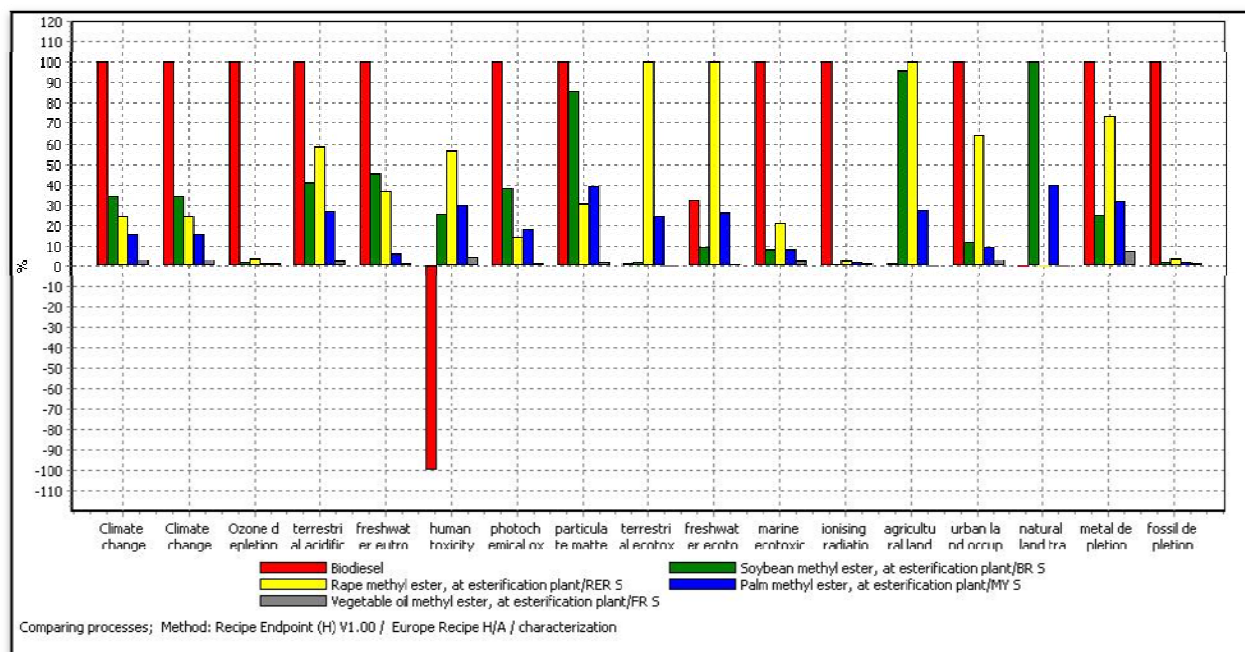


Figure 3. Relative life cycle impact (vertical axis – normalized within each impact category) analysis comparing algae biodiesel to other biodiesel processes. The poor performance of this process can be entirely attributed to the upstream burden of the glycerin (primarily methanol and natural gas used in the vegetable oil biodiesel process).

Performed economic analysis on full scale design

Although it is well known that a full scale process to produce biodiesel from algae is not economical as an industrial commercial venture with the current technology, the GREENIES team evaluated the venture as a government funded project and determined that the project is revenue neutral; i.e., the venture does not cost the taxpayers. The proposed demonstration plant provides 71 permanent, high paying jobs in addition to removing fossil fuel from our fuel mix, which reduces CO₂ emissions. The proposed capital estimate of the commercial scale plant is

summarized below. The algal growing ponds cost \$25,000,000 and the total installed cost of other equipment is \$15,000,000, giving a total capital cost of \$40,000,000. The project is essential to our economic and national security; thus, it should be financed with the sale of US Treasury Bonds bearing an interest rate of 4.00% p.a. for 30 years. After the bonds mature in 30 years, additional bonds will be sold to repay the original bondholders. The yearly interest on the bonds is \$1,620,000 and will be paid by the venture, resulting in no net cost to the US taxpayers. In addition, it is assumed that the bulk glycerol price will be \$0.06 per pound of low grade glycerol and the revenue generated by the sale of natural gas (methane) will be based on a price of \$8.00 per MMBtu. The assumption that the glycerol price will remain low is based on the fact that the market for glycerol is currently saturated and this plant will have a minimum effect on that saturation. Although the current natural gas prices are below the proposed price, as the world economic situation improves, the price of natural gas will rebound to higher levels. The proposed scenario is very sensitive to both the glycerol and natural gas prices since there is such a high volume of both of these components involved in the process.

Table 4. Estimated Capital and Operating Expenses for 1MGY facility

Capital Costs				
Equipment	Unit	Unit Cost (\$/unit)	Unit Quantity	Total Cost (\$/yr)
Algae Harvester	ea	\$250,000	5	\$1,250,000
Gravity Water Filter (Belt Conveyor)	ea	\$20,000	5	\$100,000
Centrifuge	ea	\$200,000	3	\$600,000
Parallel Plate Separator	ea	\$75,000	1	\$80,000
Methane Digester	ea	\$2,250,000	4	\$9,000,000
Biodiesel Reactor	ea	\$500,000	1	\$500,000
HP Boiler	ea	\$1,200,000	1	\$1,200,000
Turbine Generator	ea	\$250,000	2	\$500,000
Distillation Column	ea	\$250,000	1	\$250,000
Greenco-High Shear Mixer	ea	\$50,000	5	\$250,000
Vessels	ea	\$200,000	6	\$1,200,000
Agitator	ea	\$20,000	3	\$60,000
Flocculator	ea	\$90,000	1	\$90,000
Algae Ponds	ea	\$632,560	40	\$25,300,000
Total Capital Cost				\$40,400,000

Yearly Operating Costs				
Component	Unit	Unit Cost (\$/unit)	Unit Quantity	Total Cost (\$/yr)
Glycerol	lb	\$0.06	562,100,000	\$31,800,000
Methanol	lb	\$0.45	801,983	\$360,000
Hexane	lb	\$0.85	50,000	\$40,000
Boiler Feed Water	ton	\$1.10	2,190	\$2,400
Labor	ea	\$50,000.00	71	\$3,600,000
Interest on Treasury Bonds	\$	4.00%	\$40,377,400	\$1,600,000
Total Operating Cost				\$37,400,000

Yearly Revenue				
Component	Unit	Unit Revenue (\$/unit)	Unit Quantity	Total Revenue (\$/yr)
Biodiesel	gal	\$4.00	1,041,917	\$4,200,000
Methane	MMBtu	\$8.00	3,961,250	\$31,700,000
Fertilizer	ton	\$35.00	44,114	\$1,500,000
Total Revenue				\$37,400,000

Yearly Profit/ Loss = \$0.00, Process is Revenue Neutral!				
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Discussion, Conclusions, Recommendations

The GREENIES' P₃ Phase I project defines a scenario for producing fuels (biodiesel) from a renewable resource (algae) which will, with further research to improve extraction of oil from the algae, benefit people, improve economic prosperity and eventually reduce the impact of economic activity on global warming by reducing emissions of CO₂ from use of fossil fuel diesel.

The original objective of the GREENIES P₃ project was to investigate the technical and economic feasibility of utilizing a high pressure, high temperature supercritical methanol reactor to esterify, hydrolyze and transesterify fatty acids and triglycerides (the components of algae oil). This objective was achieved and, additionally, a pilot plant unit was designed for Phase II, a preliminary design was done for a full scale demonstration plant and a life cycle analysis was accomplished.

The management experiences of all team members were very beneficial to their undergraduate education, and the team was effective in using all personnel resources efficiently. The one chemistry major was very effectively used to facilitate the laboratory analytical work and demonstrated multi-disciplinary interaction.

Algae are among the most productive organism on earth to convert sunlight, atmospheric CO₂ and modest supplemental nutrients to biohydrocarbons¹. All the hydrocarbons can be readily converted to fuels, which positively impacts progress towards sustainability. This technology is applicable throughout the entire earth but is most economically applicable in tropical and sub-tropical areas. The supercritical methanol, non-catalytic reactor minimized the environmental impact of converting methanol and algae oils to biodiesel.

Partnerships have already been developed with corporations utilizing Algal Turf Scrubbing (ATS) in Maryland and Florida. Building on those relationships, students working on Phase II will work alongside Biological Engineers at the University of Arkansas to help harvest algae from a recently built ATS system in Springdale, Arkansas.

Algal Turf Scrubbers are utilized to remove excess nutrients, primarily phosphorus and nitrogen, from wastewaters and river waters. The algae are an excellent feedstock source for biofuel facilities. The proposed demonstration commercial plant will employ about 75 people in high paying jobs which are a tremendous benefit in a developed country and the reduced dependence on foreign imported petroleum feedstock speaks to national security issues.

The original focus of the project was to improve the supercritical reaction technology for converting oils to biodiesel; however, as the project progressed it became clear that the extraction of oil from algae is one of the most difficult problems encountered in converting algae oil to biodiesel. One of the innovative research aspects of this project demonstrated that glycerin is an effective agent to facilitate algae cell disruption by osmotic pressure.

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B. Proposal for Phase II

1. P3 Phase II Project Description

Challenge Definition and Relationship to Phase I

As part of the work completed in Phase I, a bench scale continuous supercritical methanol (SCM) reactor was built from commercially available components. The reactor produced biodiesel at 16mL/minute. The utilization of this robust process offers developed and developing nations the capability of producing a renewable, non-petroleum based diesel fuel. The ability of the supercritical methanol process to handle feedstocks with diverse compositions, without the use of a catalyst sets this technology apart from other biodiesel production methods. Phase I also included detailed research of feedstock options. It was desired to choose a feedstock that could offer a sustainable alternative to the use of fossil fuels and demonstrate the diversity of the supercritical methanol process. After a thorough investigation, algae oil was chosen as a feedstock because of its ability to satisfy these desires. As discovered during Phase I, algae can be used successfully to remove nutrients from polluted water streams while absorbing carbon dioxide from the atmosphere providing significant environmental benefits. The use of algae can also illustrate the importance of the supercritical methanol process because of the differing oil composition contained in the multiple different species of algae that exist.

For Phase II, the technical challenges include (1) improving the efficiency of algae oil extraction yield; (2) optimizing the reactor operation with multiple runs; and (3) finalizing a design to produce biodiesel from algae. To address sustainability implementation, students will (1) develop a economic analysis for implementation of a full scale facility (1MM gallons per year) on the Mississippi River; and (2) perform a life-cycle analysis for this facility.

Partnerships have been developed with corporations utilizing Algal Turf Scrubbing (ATS) in Maryland and Florida. Building on those relationships, students working on Phase II will work alongside Biological Engineers at the University of Arkansas to harvest algae from a recently built ATS system in Springdale, Arkansas. These students will travel to the Springdale facility, 15 miles away from the University of Arkansas campus, on a weekly basis to harvest the algae biomass. Because the quantity of biomass produced by the ATS system in Springdale is limited, algae will also continue to be collected from partners in Florida and Maryland. Mark Zivojonovich, vice president of project development at HydroMentia Inc., has agreed to supply Phase II with enough algae necessary to test and run the extraction unit that has been proposed.

Innovation and Technical Merit

After a thorough investigation during Phase I, algae oil was chosen as a feedstock because it grows steadily on any land area, it efficiently utilizes sunshine and CO₂ for growth, and its use as a fuel feedstock does not compete with food crops. The use of algae for an extraction process is extremely viable for this project because of the partnership that has been created with the HydroMentia Inc., who runs a large scale ATS system in Florida that produces 1000-3000 pounds of algal biomass weekly. The ability of the supercritical methanol process to handle diverse feedstocks, without a catalyst, was demonstrated in Phase I. The entire process to convert algae oils to biodiesel must be demonstrated in a pilot plant, which includes all the processing steps required to feed algae and end with product biodiesel. This demonstration is the primary objective of Phase II. Specific objectives in reaching this purpose include:

Objective 1: *Investigate improvements in oil extraction*

As part of Phase I, research was conducted to explore algae oil extraction methods. Based on this research, students will evaluate these extraction methods and choose the most cost effective method for the final design. This research should determine a way to increase the efficiency of oil extraction yield and develop a more effective mechanism for cell disruption.

Objective 2: *Optimize the reactor operation with multiple runs*

During Phase I, it was shown that both free fatty acids and triglycerides could be converted to biodiesel methyl esters. As part of Phase II, students will perform experimentation to optimize the reactor. This will include determination of flowrates, oil to methanol ratio, free fatty acid to triglyceride ratio, temperature, and pressure giving the highest yield.

The process flow schematic for Phase II is shown in Figure 4. Cell wall disruption is accomplished by osmotic shock by blending the wet algae feed with ½ volume of 8 molar (42 wt %) glycerol solution. Mechanical agitation is required to disperse the algae strands and clumps and assist cell disruption and will be provided by a 2 HP garbage disposal (Insinkerator SS- 200). 24 gallons of wet algae and 12 gallons of glycerol solution are added to the 55 gallon algae mix tank. The mix tank batch will be circulated (for 60 minutes, giving 17 tank turnovers) from the tank through the Insinkerator with a 10 gpm positive displacement circulating pump. Two extraction batches will be handled per day. The separation of the hexane phase from the aqueous phase cannot be accomplished by gravity separation alone. The separation will be accomplished in the pilot plant by using a clothes washer which can achieve approximately 340 g; 8 centrifuge batches will be required per day.

After the separation, the hexane will be at the air interface, the clarified aqueous phase will exist below it, and the spent algae will be caked on the walls of the washer bowl. The washer will be stopped, and the water and hexane phases will be pumped into the 50 gallon hexane-water separator. After 30 minutes for separating, the water phase will be decanted from the vessel and disposed. The decanted hexane phase - about 6 gallons produced per day - will be drained into a forced-circulation vaporizer. The hexane vapor exits the top and is condensed in ½" OD by 190" copper tubing. About 1 gpm of cooling water will flow thorough a PVC shell to perform the condensing. The condensed hexane flows by gravity to a hexane storage tank. After the hexane removal, the batch of algae oil is transported to the reactor oil feed tank.

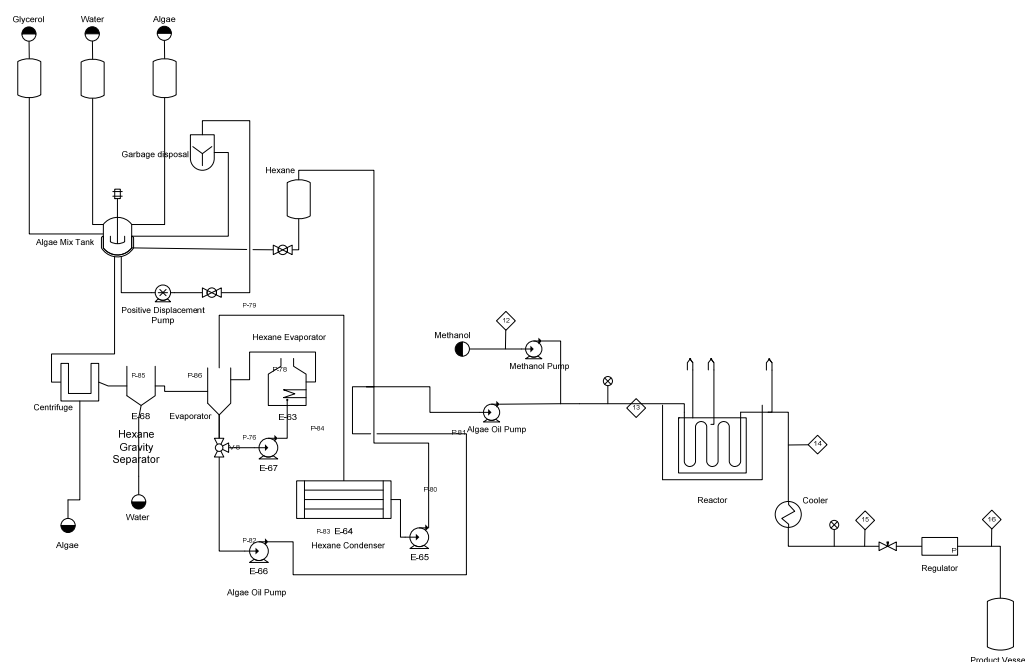


Figure 4. Phase II Process Flow Schematic

Objective 3: *Finalize the design of a full scale demonstration biodiesel facility*

The full scale process involves the following three steps.

In the first step of the process, algae are produced via the Algal Turf Scrubbing (ATS) system. This system, invented by Walter Adey, a scientist and curator of the Smithsonian Institute, is a solar/algal technology that utilizes filamentous algae of many genera and species to capture the energy of sunlight and build algal biomass from CO_2 ¹. Algal communities grow on mesh screens, using sunlight as an energy source helping to preserve limited resources. The ATS system is highly effective in capturing nutrients from a wide variety of waste and industrially-polluted waters¹. After treatment, the water can be discharged back into the river, full of oxygen and meeting environmental regulations. Many toxic organic compounds can be degraded with ATS systems by combining algal-produced oxygen at super-saturated levels with solar energy¹. ATS also produces a low cost, harvestable algal biomass at an order of magnitude greater rate than agricultural and forestry products at the same latitude¹. This biomass can be used in biodiesel production.

The second step of the process includes harvesting the algal biomass from the ATS system and extracting the oil from the algal cell walls. Depending on the season, the algal turf biomass must be harvested every 5 to 15 days to maintain high levels of productivity². The Algal Turf Scrubbers are more productive than terrestrial crops, with mean yearly rates in the central U.S. being 30-40g (dry)/m²/day. Traditional crop production in the U.S. is 2-4g (dry)/m²/day. At the same levels of light, algae can photosynthesize and produce new tissue at roughly 10 times that of typical crops². After the oil has been extracted from the algal cells, the spent algal biomass is left. This biomass is degraded by an anaerobic digester producing methane for electricity, carbon dioxide which is fed to the algae, and fertilizer used for irrigation.

The third step of the process includes converting the extracted oil into the desired biodiesel product using the supercritical methanol technology. The process subjects the reactants

to high temperature (350°C) and high pressure (2000 psi), which allows the methanol to become an effective solvent that dissolves the oil in one step, without the use of a catalyst. This process provides a renewable, biodegradable fuel source that decreases sulfur and particulate-matter emissions and reduces the United State's dependence on foreign oil¹⁷. Biodiesel also provides lubrication for better-functioning mechanical parts and has excellent detergent properties¹⁷. The use of algae oil for the production of biodiesel not only has the ability to lessen carbon emissions, but this process also completes the carbon cycle as the limiting amount of carbon emitted into the atmosphere by diesel engines is recaptured by the algae.

Based on this technical design for the full scale system, a life-cycle analysis and an economic analysis can be conducted. A class 4 cost estimate, 1-15% accuracy level, was calculated as part of Phase I. Phase II students will perform a class 2 cost estimate, 30-70% accuracy level for implementing a full scale plant on the Mississippi River. A life-cycle analysis, including all energy and carbon required to build and operate the system, will be conducted. The life-cycle analysis will offer calculations demonstrating the exact benefits this process can provide. In addition, a detailed analysis of the regulatory environment in which the project will be implemented will be performed. This includes a determination of all waste streams produced, and an analysis of acceptable disposal for those wastes.

Relationship of Challenge to Sustainability (People, Prosperity, and the Planet)

Increasing demand for energy in the developed and developing worlds paired with diminishing natural resources calls for a sustainable, renewable process such as the production of biodiesel from a viable feedstock such as algae. The integration of an oil extraction unit with the supercritical methanol reactor built in Phase I, has the potential to sustain environmental protection, economic prosperity, and social benefit.

This process has the ability to sustain environmental protection by utilizing the ATS system for algae production. With the integration of the ATS system in the project, the algae feedstock serves two important purposes. First, the algal communities are used to reduce nitrogen and phosphorous concentration in water streams. The algae use sunlight and unwanted CO₂ from the atmosphere to flourish. By using the sunlight, algae employ a natural energy source for reproduction as opposed to other feedstocks that require energy produced by fossil fuels. Algae also grow by absorbing CO₂ from the environment, thus reducing the amount of greenhouse gases existing in the atmosphere, which is of increasing global and local concern. Secondly, the algal biomass, which must be harvested frequently in order to maintain a healthy growing habitat, can be further used as biodiesel feedstock.

In addition to environmental protection, this process promotes economic prosperity. As the United States finds a need to lessen its dependency on foreign oil, bio-fuel production will increase. This has the potential to create domestic labor and market opportunities. The implementation of bio-fuels could eventually compete with petro-diesel products, helping regulate the prices of fuel. As natural resources continue to diminish, future generations will be forced to rely on a renewable fuel source. By making advancements in this technology now, we can aid future generations in refining the process and creating a marketable product.

The overall process also provides social benefit. A full scale design, implemented to clean up the Mississippi River, has the ability to provide approximately 75 jobs to people in low income areas for operation of the facilities. The local diesel providers can also benefit from buying the diesel directly from the production facilities at a lower cost. Considering society as a

whole, the benefit of creating a sustainable fuel source that does not compete with food or any other outside industries is not only desired but continues to become more of a necessity.

Measurable Results (Outputs/Outcomes), Evaluation Method, and Implementation Strategy

For Phase II, the ultimate goal is to build an algae oil extraction system and prepare detailed economic and life-cycle analyses. Phase II can be considered successful as long as the project is able to sustain environmental protection, economic prosperity, and social benefit. As part of environmental protection, all product streams and waste streams should be equally as environmentally friendly, if not more, when compared to currently used products.

Since an adequate amount of research has been performed as part of Phase I, there should be a smooth transition into the work proposed for Phase II. Partnerships that were developed as part of Phase I, have agreed to continue supporting Phase II plans.

Integration of P3 Concepts as an Educational Tool

This P³ project will be used to satisfy the requirements of the chemical engineering capstone senior design course. While this project more than satisfies these requirements, which include performing heat and mass balances; preparing process flow diagrams; designing, scaling-up and costing process equipment; performing economic analysis and using the latest and best process simulators. This competition will allow the students to obtain extremely valuable experience with laboratory experimentation, which is not a normal part of the capstone design. The hands on experience of designing and building experimental equipment apparatuses from scratch, conducting experiments, analyzing samples and presenting results are part of the invaluable experience which this P³ project offers.

2. Project Schedule

Task Schedule									
	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
Objective 1: <i>Investigate Extraction</i>									
Objective 2: <i>Optimize Reactor</i>									
Objective 3: <i>Finalize Design</i>									
Primary Objective: <i>Full Scale Design</i>									

The development of this project will require multiple disciplines. Although the senior design course, through which this process will be developed, is only open to Chemical Engineers, students from different areas of study with extensive knowledge of algae would provide a significant resource for the development of a system to extract algae oil. Biochemical Engineers who work with the local ATS system would also provide a wealth of knowledge in the further design of a full scale operational unit.

3. Partnerships

Vital partnerships have been made for aiding in the completion of Phase II:

HydroMentia, Inc.: HydroMentia is an engineering and technology firm that provides natural, cost-effective, and sustainable water treatment technologies. This company, which holds the industrial license for the Algal Turf Scrubber (ATS), has developed and expanded ATS systems for the economic removal of nutrients from large bodies of water. Working with Mark Zivojnovich of HydroMentia, students will be able to produce a full scale design based on the use of the ATS system to produce the algae needed to create biodiesel. HydroMentia has also agreed to supply the project with enough algae needed to thoroughly test the extraction unit that will be constructed during Phase II of the competition.

Marty Matlock: Marty Matlock, associate professor in the department of biological and agricultural engineering at the University of Arkansas, was recently awarded a National Science Foundation REU (Research Experience for Undergraduates) grant for assessment and sustainable management of ecosystem services. As part of the grant, an interdisciplinary group of students have started work on a project sponsored by the Smithsonian Institute's Museum of Natural History. The goal of the project is to evaluate the feasibility of producing algal biomass for biofuels and reducing nutrient contaminants in streams. Matlock has agreed to allow students participating in Phase II of this competition to work alongside biological engineering students in harvest the algal biomass, which will be used in the proposed algae oil extraction unit. The P3 project will synergize with the current NSF and Smithsonian efforts to provide a more complete solution.